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ABSTRACT (Continue as reverse side if necessary and identify by block number)

→An investigation was made of a number of tettering techniques particularly important for VLSI processing. These techniques have included back surface gettering, intrinsic gettering, and HCl oxidation.

The general approach of the investigation was to concentrate on the fundamental mechanisms involved with each of the gettering techniques, looking not only at the electrical implications of the technique, but also at the chemical and microstructural properties

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ELECTRICAL, CHEMICAL, AND MICROSTRUCTURAL CHARACTERIZATION OF GETTERING MECHANISMS FOR VLSI

FINAL REPORT
Submitted by
Joseph R. Monkowski

January 31, 1984 SEPTEMBER 1983

U.S. ARMY RESEARCH OFFICE

Contract Number DAAG29-80-K-0085

THE PENNSYLVANIA STATE UNIVERSITY DEPARTMENT OF ELECTRICAL ENGINEERING

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INTRODUCTION

In this program, we have investigated a number of gettering techniques particularly important for VLSI processing. These techniques have included back surface gettering, intrinsic gettering, and HCl oxidation.

The general approach of the investigation was to concentrate on the fundamental mechanisms involved with each of the gettering techniques, looking not only at the electrical implications of the technique, but also at the chemical and microstructural properties. Consistent with this approach, we have attempted to go beyond the individual gettering techniques, and have instead looked more broadly at the various mechanisms associated with each of the techniques. For example, the investigation dealing with HCl oxidation has led to an extensive modelling of the chlorine incorporation, ^{1,2} additional phase formation, ³ and metallic impurity removal; ^{4,5} the investigation dealing with intrinsic gettering grew to a much larger study involving the interaction between oxygen and point defects in the silicon; ⁶⁻⁹ and an investigation dealing with measurement of oxidation - induced stress has ultimately resulted in a new proposed model for the growth and shrinkage of stacking faults. ¹⁰

Each of these areas is briefly reviewed below. Since a more thorough coverage can be found in the appended papers, this part of the report has intentionally been kept brief, with only the highlights being discussed.

HC1 GETTERING OF CRYSTALLINE DEFECTS AND IMPURITIES

Thermal oxidation of silicon in the presence of HCl is a very common techniques used for obtaining a number of benefits in both MOS and bipolar processing. Some of the most significant benefits include the gettering of metallic impurities from the silicon, resulting in greatly improved minority carrier lifetimes; and the shrinkage of stacking faults.

We have used secondary ion mass spectrometry (SIMS) in conjunction with electron microscopy to establish that the chlorine is incorporated into an additional phase at the oxide/silicon interface. Subsequent thermodynamic analysis led the way to the development of a model that quantitatively describes the phase formation in terms of the ratio of chlorine activity to oxygen activity at the oxide/silicon interface. Although the main use of the model is in the choice of appropriate oxidation conditions, e.g. HCl concentration, oxidation time, and oxidation temperature, the model has also been used very effectively to predict and prevent situations that could lead to catastrophic failure of the fabricated devices.

We have also studied the effectiveness of chlorine in the gettering of metallic impurities from silicon. Atomic absorption spectroscopy has clearly shown differences in the ability of the chlorine to remove different metals from the silicon wafer. For example, we have found that whereas copper is readily removed from a wafer during an HCl oxidation, gold is completely unaffected. These differences have been explained in terms of differences in the chemistry of the various metal chloride systems.

The electrical implications of HCl processing were studied with deep level and minority carrier lifetime measurements. One of the major findings from this investigation was that although the HCl processing improves the carrier lifetime as anticipated, there is not the relationship between carrier lifetime and deep level measurements that is typically expected. Further work needs to be done to establish the origin of the discrepancies.

INTRINSIC GETTERING AND THE BEHAVIOR OF OXYGEN IN SILICON

As a result of its use in intrinsic gettering, the behavior of oxygen in silicon has become of great interest. In particular, the out-diffusion of oxygen, which results in the formation of the denuded zone, and the precipitation of oxygen, which results in the formation of the gettering sites, have been especially investigated.

We have used secondary ion mass spectrometry to study the out-diffusion of oxygen, and have noted a clear dependence of the diffusivity on the processing ambient. For example, an HCl oxidation results in a diffusivity significantly higher than that found for a steam oxidation. The general conclusion developed from these results was that point defects play a large role in the diffusion of oxygen, and in particular, oxygen diffuses via a vacancy-dominant mechanism.

We have also established that in addition to the large role played by point defects in the diffusion of oxygen, point defects also significantly affect the precipitation of oxygen. In fact, this dual role of point defects lends a large amount of flexibility to the use of intrinsic gettering. For example, by appropriate choice of processing ambients designed to control the point defect situation in the silicon, one can control the width of the denuded zone within a relatively wide latitude.

Atomic absorption spectroscopy was used to determine the effectiveness of oxygen precipitates in the gettering of metallic impurities. In general, we found that the precipitates are very effective gettering sites, but the situation is not as straightforward as typically believed. Often, there were precipitates in the middle of the desired denuded zone, leading to the presence of metallic impurities very close to the active devices.

The anomalies were attributed to grown-in defects in the silicon wafer. 9

BACK SURFACE GETTERING

A new back surface gettering technique has been invented and a patent disclosure prepared. We have shown the technique to be very effective in removing both metallic impurities and crystalline defects from the active device regions. Further work is being carried out on the technique and a number of interested parties are reviewing the disclosure.

OXIDATION-INDUCED STRESS

Mechanical stresses generated during the thermal oxidation of silicon have been measured in situ for oxidations performed in dry 0_2 , H_20 , and 6% HCl/ 0_2 at temperatures of 800° -ll00°C. In general, the data clearly fit a model based on viscoelastic flow of the oxide. Comparison of experimental data with theoretical calculations shows a very good fit. 10

As anticipated, for each ambient there exists a particular temperature above which the growing oxide is essentially stress-free. Furthermore, this temperature is higher for the dry 0_2 oxides than for the $\rm H_2O$ and HCl oxides.

A particularly interesting possibility that we propose is that through a form of Nabarro-Herring creep, the stresses are responsible for the injection of silicon self-interstitials into the silicon crystal. If this hypothesis is correct, the stresses could be instrumental in the formation of oxidation-induced stacking faults. Furthermore, it may be the stress relaxation during an HCl oxidation that allows for the shrinkage of stacking faults.

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The following researchers have been associated with this program:

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